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The Electro-Chemistry of Soil Formation: I. The Gel and the Sol Complex.

By SANTE MATTSON and YNGVE GUSTAFSSON.

From the Department of Soil Science of the Agricultural College of Sweden, Upsala.

Introduction.

The soil colloids represent salts of weak acids and bases, principally silicic and humic acids and the hydrous oxides of aluminum and iron. They react therefore amphoterically, combining with other acids and bases and, by ion exchange, with anions and cations in general. They differ however from true ampholytes in that their acidic and basic groups exist as discrete parts in the colloidal salt complex. They are therefore subject to hydrolytic decomposition, splitting off either one of the two kinds of groups, all depending upon the pH of the medium and the ionization of the groups. The isoelectric point, at which the complex is most stable, is determined by the relative quantities and activities of the acidic and basic groups. Above this pH the colloid dissociates an anion complex, which is richer in acidic groups and poorer in basic groups than the original colloid, whereas at a pH below the isoelectric point, a cation complex is dissociated, which is richer in basic groups and poorer in acidic groups than the original or parent complex. In a preceding work (MATTSON & NILSSON, 1935) we designated the former the *anionic sol complex* and the latter the *cationic sol complex* as distinguised from the *gel complex*, from which they are split off by a hydrolytic cleavage. Because of the strong charge

and the resulting high degree of hydration the sol complexes assume a more or less high degree of dispersion.

In the work referred to we were able to give a satisfactory explanation of the dispersion and precipitation within the podzol profile. The facts established were in complete accordance with the laws of isoelectric precipitation and with the theory of isoelectric weathering (MATTSON, 1932). But the limited conditions of our former experiments were such, that we could only predict, but not show, the important fact that, even in the case of the natural soil material, there must be a minimum in dispersibility at a pH which corresponds to the isoelectric point. For this reason, and because of the great importance of the problem in general, we have continued the experiments on a larger scale by investigating the influence of the pH, over a wide range, on the ionization and dispersion of the acidic and basic constituents of each system of soil materials.

In this as in the previous work we have studied mixtures of humus and mineral soil material from the B horizon of a podzol profile. We shall later give an account of the results now obtained in a study of systems containing humus together with salts of aluminum, ferric and ferrous iron, and manganese. It is our plan to continue this study of the stability of various soil complexes at different hydrogen ion concentration, with and without the influence of various ions, and to include in this work materials from the different soil types such as the podzols, brown soils, red earths, laterites, tshernosems and others. Because of the large scope and special nature of this investigation we have decided to start a new series under the title »the electro-chemistry of soil formation». All chemistry is, of course, in its last analysis, electro-chemistry, but the methods here applied deal specifically with the electro-kinetics of the soil colloidal complex. The term is therefore appropriate in this connection.

It is our conviction that a deeper insight into the processes of soil formation must be based on a much wider knowledge

of the reactions and behavior of the various soil colloids than we now possess. We have too long been applying quantitative methods to materials whose qualitative reactions have been very little understood. The qualitative chemistry of the ordinary ions finds very little application in the study of the soil colloidal complex. The soil chemist must develope his own qualitative chemistry of the soil. Let us explain with an example: The rate of weathering has been assumed (POLUINOV, 1930) to be much greater for the anions Cl and SO_4 than for the ordinary cations. This is not always true. It is true for soils whose colloidal complex has a low isoelectric point and whose pH is relatively high. The complex functions then as an acid and binds the cations, thus protecting them from a rapid leaching. It is not true for a soil whose complex has a high isoelectric point and whose pH lies at or below this point. The SO_4 ion, especially, is then firmly bound by the complex, which, in a large measure, functions as a base. Thus many laterites, which contain little or no exchangeable cations, contain considerable quantities of displaceable SO_4.

We are directing our efforts to a study of how the soil complex reacts and behaves. We shall not try to explain its chemical constitution and structure, for we do not believe that the *reactive* material in soil colloids possesses a definite composition and structure. The fact that soil colloids, organic and inorganic, interact mutually with each other as well as with all electrolytes which happen to get into the soil solution and, further, the fact that their products of decomposition varies with the pH, shows that they cannot be compounds of definite composition. To assign a formula to a complex whose identity as a chemical body changes with the conditions would obviously be meaningless, and

»If there is no meaning in it» said the King, »that saves us a world of trouble, you know, as we need'nt try to find any» — LEWIS CARROLL, in *Alice in Wonderland.*

By this we do not mean that the soil colloids do not contain definite compounds having a definite crystal structure.

We consider it quite evident that certain crystalline compounds are formed under different conditions. Thus the clay minerals of the montmorillonite and beidellite type appear to be formed from the slightly leached products of hydrolysis, which contain a high proportion of silica and bases, whereas the more strongly leached, unsaturated and acidic products of hydrolysis seem to favor the formation of minerals such as kaolinite and halloysite. A more complete leaching of the silica, finally, seems to favor the formation of gibbsite, limonite and other compounds of this type. But these crystalline compounds of definite composition represent frozen matter, so to speak. The chemically active material of soil colloids is represented by the surface layer of ions on these crystals and by the noncrystalline gels.

Some of the soil scientists, who have directed their efforts to a study of crystal structure, would explain base exchange as a function of a particular structure (MARSHALL, 1935). Their reasoning is that the cations in the lattice are displaced by other cations, without otherwise altering the composition of the alumino-silicate. It is on the basis of this simple reaction that their conception of, definitely composed, cation exchange silicates rests. They forget that the reactivity of the colloidal complex is not limited to an exchange with the common cations but includes all ions, colloidal aggregates as well as single ions, not to mention polar group in general. Suppose that the positive ion, i.e. Al, in the surface layer binds a phosphate, a silicate or a humate ion, or that one of the common cations is displaced by the ion $Al(OH)_2^+$ or $Fe(OH)_2^+$, which thereby becomes attached to the silica layer. The composition of the interior of the crystal is still the same, but the composition and properties of the surface layer have obviously been changed. The acidoid/basoid ratio in the reactive material is increased in the first case and reduced in the second. This explains the increase in the cation exchange of a laterite by a treatment with phosphate (MATTSON, 1931 c) and

why the exchange power of bentonite was found to be reduced by aluminum hydroxide (MATTSON, 1931 b).

It is obvious that the composition of the crystal as a whole is no expression of the composition of the reactive material. The acidoid/basoid ratio must therefore express the activities and not the masses if we are to relate this ratio to the properties. In our opinion the cation and anion exchange is conditioned by the activities of the acidic and basic groups of the colloid and is only modified by its structure.

It is this relationship between the acidic and basic activities of the material which enables us to undertake a systematic study of the behavior of soil colloids even then, when we are entirely ignorant of composition and of structure. Let it be a mineral gel of the most indefinite composition or let it be the most complex of all terrestrial matter, the humus, its most important function as a chemical entity will be an orderly expression of the relative activities of its acidic and basic groups. As long as we study the soil colloids from this standpoint we shall escape the disillusionment predicted by the writer of Monthly Letter No. 58, Imperial Bureau of Soil Science, when he says: »*If a research worker seeks early disillusionment or wishes to propound an untenable theory, let him study humus.*«

Colloidal acids, bases and salts.

The colloidal condition of the soil acidoids and basoids does not prevent them from reacting in the same manner in which ordinary acids and bases react. The difference between colloidal and ordinary electrolytes is primarily a difference in degrees, not in kind. Electrolytes exist in all degrees of dispersion, the »true« solution of ordinary electrolytes representing the ultimate state of dispersion.

We can, however, not apply the mass law to colloidal electrolytes for we have no way of telling their concentration or reacting masses, which is greatly modified by their state of

aggregation. Another distinction of colloidal electrolytes is, that not only the acidoids and basoids but also their salts (the saloids) undergo a limited degree of dissociation. Another important distinction is that there is no stoichiometry in the colloidal complex beyond a balance between positive and negative ions. Any proportion of acidoid and basoid my enter into the make-up of the complex, and the saloid may exist in association with various proportions of its products of hydrolysis, in so far as these remain in the colloidal condition. There is no such a thing as a pure colloid. The term is meaningless, for any attempt to purify a colloid changes its identity. We might as well attempt to purify living matter.

The colloidal acids and basis in the soil complex may be very weak and yet, because of the low dissociation of their salts, may possess a considerable power to combine mutually with each other and with other acids and bases or with their anions and cations. This is illustrated in fig. 1 *a*.

The unbroken curve in the figure represents the dissociation residue or uncombined part of a monobasic acid, whose dissociation constant $K_a = 10^{-7}$, when combining with a base with which it forms a completely dissociated salt. The dissociation residue p is calculated by the equation

$$p = \frac{1}{1 + \frac{K_a}{(H^+)}}$$

and is about 99 % at pH 5, 50 % at pH 7 and about 1 % at pH 9.

If, however, the reaction takes place in the presence of a cation I^+ with which the acid anion forms a slightly dissociated salt, then the power of the acid to neutralize base will be increased. The acid will act as if it were a stronger acid, its apparent dissociation constant being greater than its true constant.

For the case that the cation I^+ is present in sufficient excess, so that its interaction with the acid does not materially

affect its concentration Michaelis (1926) derives the following expression for the dissociation residue

$$p = \frac{1}{1 + \frac{K_s}{(H^+)}\left(\frac{i^+}{K_s} + 1\right)}$$

where i^+ is the concentration of the cation and K_s the dissociation constant of the salt.

If we assume that $i^+ = 0.1$ N and that $K_s = 0.001$ and calculate p at different hydrogen ion activities we obtain the broken curve in fig. 1 *a*. The position of the curve would be the same for $i^+ = 1.0$ N and $K_s = 0.01$ or any other set of values whose ratio $\frac{i^+}{K_s} = 100$.

The effect of the presence of the cations will, in the assumed case, be the same as if the dissociation constant of the acid were 10^{-5} instead of 10^{-7} ($pK = pH$ at $p = 0.5$).

A practical example of the effect of true salt formation is shown in fig. 1 *b*. The curves were obtained by titrating 1 millimol H_3PO_4 by NaOH and by $Ca(OH)_2$ in a constant volume of 105 cc. Due to the formation of a slightly dissociated (a precipitated) calcium salt, two of the hydrogen ions of the acid »neutralize» $Ca(OH)_2$ at a much lower pH than NaOH. The dissociation constants of H_3PO_4 at 25° C are 1×10^{-2}, 8.8×10^{-8} and 3.6×10^{-13} for the first, second and third stage respectively. The apparent, second and third constants are much greater when the acid combines with $Ca(OH)_2$ (or with NaOH in the presence of Ca ions).

We have previously applied this principle to an explanation of the fact that soil colloids bind more base at a given pH in the presence of a neutral salt than in pure water. Thus a certain soil, which at pH 7.0 binds 6.8 m. e. NaOH in the absence of salt, binds 8.1, 11.7 and 16.0 m. e. base in 0.01, 0.1 and 1.0 N solutions of Na_2SO_4 respectively (Mattson & Gustafsson, 1935 b), *The lower the dissociation of the salt which a cation*

forms with an acid anion the more successfully do the cations compete with, and displace the H ions of the acid, and the stronger does the acid appear to be. The same is true of a base.

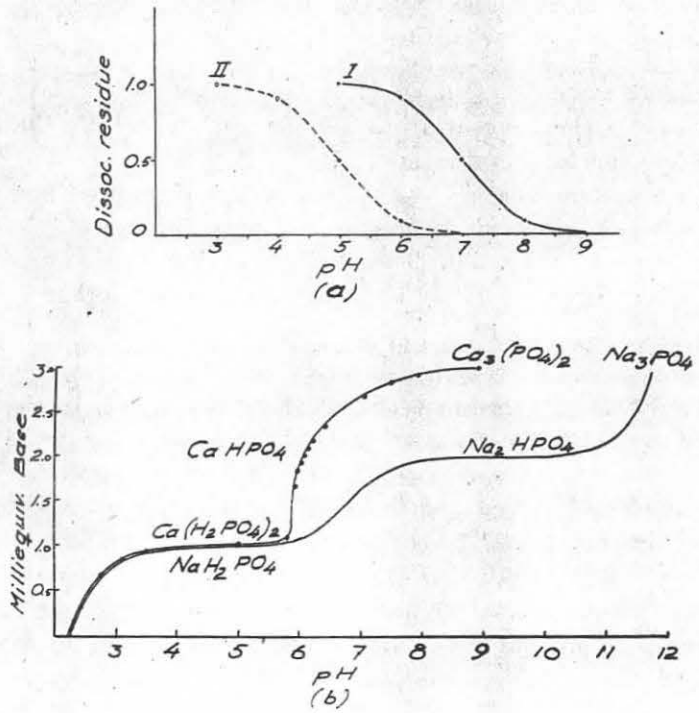


Fig. 1.

(*a*) I. The dissociation residue of an acid whose dissociation constant $= 1 \times 10^{-7}$.

II. The same in the presence of a certain concentration of a cation with which the acid forms a slightly dissociated salt.

(*b*) The titration of 1 m.mol H_3PO_4 (in 105 cc.) by $Ca(OH)_2$ and NaOH.

In order to illustrate the interaction of colloidal acids and bases let us begin with a tri-acidic base, $B(OH)_3$, with the apparent dissociation constants $k_{b_1} = 10^{-7}$, $k_{b_2} = 10^{-8}$ and $k_{b_3} = 10^{-9}$. The capacities y_1, y_2, y_3 to bind acid are calculated from the equation

$$y = \frac{c}{1 + \frac{(OH^-)}{k_b}}$$

where c = concentration of the base. Putting c = 1 we get approximately the values given in table 1 (A). By plotting Σy against pH we obtain the left side curve in fig. 2 *a*. At pH 9 the base binds about 0.01 equivalent of acid, and at pH 3 it has combined with approximately 3.0 equivalents of acid.

Since the base is colloidal it will pass through three forms of aggregation between pH 9 and 3 as follows:

(1) the gel form,
(2) the sol form,
(3) »true» solution.

In the uncombined state the base will exist in the gel condition as $[B(OH)_3]_n$. This is indicated by the full-drawn section of the curve. As the base combines with an acid, i. e., HCl etc., with which it forms a dissociating salt, it becomes ionized, and changes gradually to the sol condition, in which the base exists as $[B(OH)_2^+]_n$ or $(BOH^{++})_n$ or any mixture of these. This is indicated by the broken section of the curve. Finally the base becomes fully ionized as B^{+++}, and passes into »true» solution as indicated by the dotted section of the curve.

Since the base must be assumed to react amphoterically, like the weak soil bases aluminium and iron hydroxides, it must possess an isoelectric point. If we assume its apparent acid dissociation constants to be $k_{a_1} = 10^{-9}$, $k_{a_2} = 10^{-10}$ and $k_{a_3} = 10^{-11}$ and calculate the capacities x_1, x_2, x_3 to bind base from the equation

$$x = \frac{1}{1 + \frac{(H^+)}{k_a}}$$

we get the right hand curve in fig. 2 *a* as an expression for Σx. The amphoteric hydroxide would, therefore, be isoelectric at pH 8, for here it combines with equal quantities of acid

Table I.

Capacity to bind acid when $k_{b_1} = 10^{-7}$, $k_{b_2} = 10^{-8}$, $k_{b_3} = 10^{-9}$

(A) c = 1 mol base

(H+) / (OH−)	10^{-2} / 10^{-12}	10^{-3} / 10^{-11}	10^{-4} / 10^{-10}	10^{-5} / 10^{-9}	10^{-6} / 10^{-8}	10^{-7} / 10^{-7}	10^{-8} / 10^{-6}	10^{-9} / 10^{-5}	10^{-10} / 10^{-4}
y_1	1.00	1.00	1.00	.99	.91	.50	.09	.01	
y_2	1.00	1.00	.99	.91	.50	.09	.01		
y_3	1.00	.99	.91	.50	.09	.01			
Σy	3.00	2.99	2.90	2.40	1.50	.60	.10	.01	

Capacity to bind base when $k_{a_1} = 10^{-5}$, $k_{a_2} = 10^{-6}$, $k_{a_3} = 10^{-7}$

(B) c = 0.1 mol acid

x_1		.001	.009	.050	.091	.099	.100	.100	.100
x_2			.001	.009	.050	.091	.099	.100	.100
x_3				.001	.009	.050	.091	.099	.100
Σx			.01	.06	.15	.24	.29	.30	.30
$\Sigma x - y$	−3.00	−2.99	−2.89	−2.34	−1.35	− .36	.19	.29	.30

(C) c = 0.5 mol acid

x_1		.005	.045	.250	.455	.495	.500	.500	.500
x_2			.005	.045	.250	.455	.495	.500	.500
x_3				.005	.045	.250	.455	.495	.500
Σx		.005	.05	.30	.75	1.20	1.45	1.50	1.50
$\Sigma x - y$	−3.00	−2.98	−2.85	−2.10	− .75	.60	1.35	1.49	1.50

Table I (cont.).

(D) c = 1.0 mol acid

(H+)	10^{-2}	10^{-3}	10^{-4}	10^{-5}	10^{-6}	10^{-7}	10^{-8}	10^{-9}	10^{-10}
(OH−)	10^{-12}	10^{-11}	10^{-10}	10^{-9}	10^{-8}	10^{-7}	10^{-6}	10^{-5}	10^{-4}
x_1		.01	.09	.50	.91	.99	1.00	1.00	1.00
x_2			.01	.09	.50	.91	.99	1.00	1.00
x_3				.01	.09	.50	.91	.99	1.00
Σx		.01	.10	.60	1.50	2.40	2.90	2.99	3.00
$\Sigma x-y$	−3.00	−2.98	−2.80	−1.80	±0.0	1.80	2.80	2.98	3.00

and base. The described hydroxide would resemble aluminum hydroxide, which has been found to be isoelectric at pH 8.1, when precipitated from the chloride by NaOH.

We shall now consider the interaction of the colloidal hydroxide with varying proportions of a tribasic colloidal acid, H_3A, with which it forms a slightly dissociated, colloidal salt. We shall assume that the acid, when reacting with the hydroxide, possesses the apparent constants $k_{a_1} = 10^{-5}$, $k_{a_2} = 10^{-6}$, $k_{a_3} = 10^{-7}$.

In order to simplify the relationship we shall only consider the basic function of the hydroxide (y values), and ignore its function as acid (x values), not forgetting, however, that at pH above 8 the hydroxide does function as an acid and binds base.

Table I (B), (C), and (D) give the capacities, x_1, x_2, x_3, of 0.1, 0.5 and 1.0 mol of the acid H_3A to bind base respectively. The Σx values of 0.1, 0.5 and 1.0 mol acid are plotted together with the Σy values of 1.0 mol of the hydroxide in fig. 2 *b*, *c* and *d* respectively.

The $\Sigma x-y$ values in the table show the *net* capacities of the different combinations to bind acid (negative values) and base (positive values), and are represented in the figures by

the vertical distance between the two curves; the negative values on the left and the positive values on the right. The pH at which $\Sigma x - y = 0$ corresponds to the point of intersection of the curves, and represents the isoelectric point of the complex.

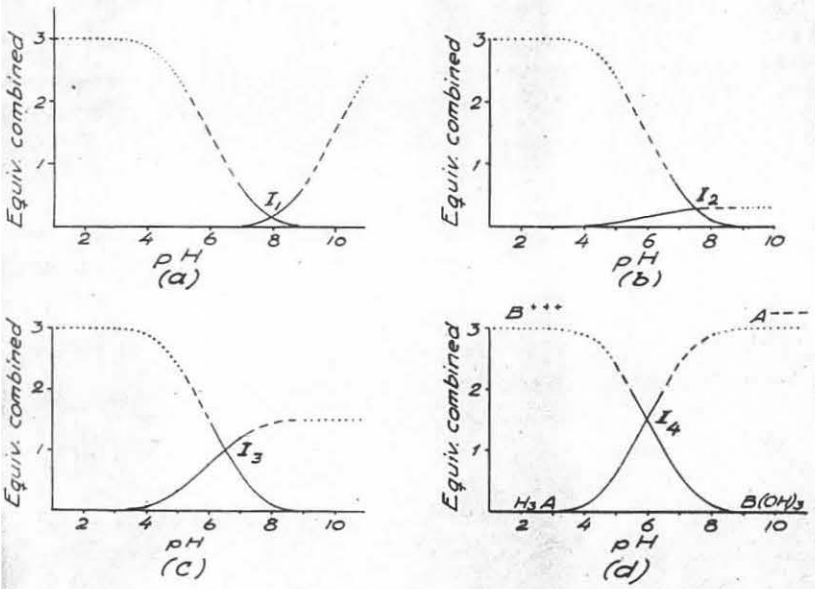


Fig. 2. The capacities to bind acid (left side) and base (right side) and the isoelectric point I of colloidal systems containing:

(*a*) an amphoteric hydroxide $B(OH)_3$ ($k_{b_1} = 10^{-7}$, $k_{b_2} = 10^{-8}$, $k_{b_3} = 10^{-9}$ and $k_{a_1} = 10^{-9}$, $k_{a_2} = 10^{-10}$, $k_{a_3} = 10^{-11}$).

(*b*), (*c*) and (*d*). One mol of the hydroxide $B(OH)_3$ (basic function) and 0.1, 0.5 and 1.0 mol respectively of an acid H_3A ($k_{a_1} = 10^{-5}$, $k_{a_2} = 10^{-6}$, $k_{a_3} = 10^{-7}$). k = apparent dissociation constant (comp. table 1).

We note that the addition of increasing amounts of the acid H_3A to a given amount of the hydroxide leads to:

(1) a decrease in the power to bind acid, and to exchange anions, within a certain range of reaction, in which the added acid has tied up a certain amount of the hydroxide, thus leaving a smaller basic residue;

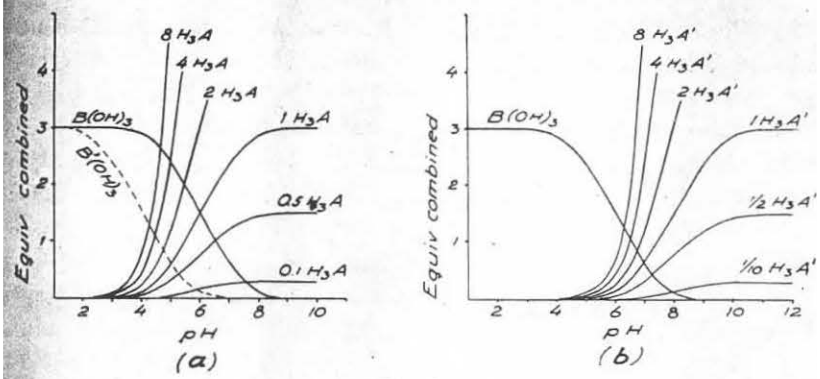


Fig. 3.

(*a*) One mol $B(OH)_3$ in combination with 0.1 to 8 mols H_3A. (Comp. fig. 2). $B'(OH)_3$ represents a weaker hydroxide.

(*b*) One mol $B(OH)_3$ in combination with 0.1 to 8 mols of a weaker acid, H_3A' ($k_{a_1} = 10^{-7}$, $k_{a_2} = 10^{-8}$, $k_{a_3} = 40^{-9}$).

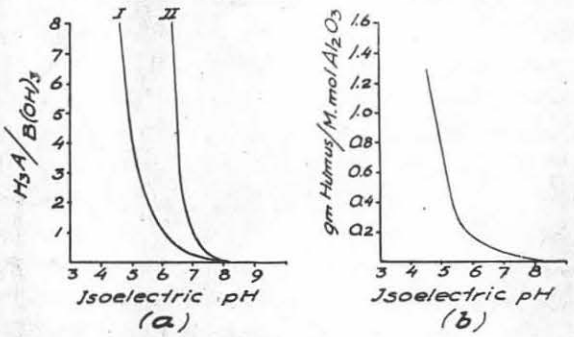


Fig. 4.

(*a*) **The relationship between the ratio $H_3A/B(OH)_3$ and the isoelectric point. Curve I is based on fig. 3 (*a*) and curve II is based on fig. 3 (*b*).**

(*b*) **The corresponding relationship in an isoelectrically precipitated Al-humate series.**

(2) an increase in the power to bind base, and to exchange cations, due to an increment in the acidic residue of the complex;

(3) a deflection of the isoelectric point to the acid side, and consequently a stabilization of the complex in the same direction.

In order to illustrate the effect of a further addition of acid fig. 3 *a* is presented, which shows the position and intersection of the curves up to 8 mols of H_3A to 1 mol $B(OH)_3$. From the position of the curves it is evident that the deflection of the isoelectric point becomes smaller, gradually approaching a limit as we increase the amount of acid. This relationship is brought out more clearly by plotting the molar ratio $H_3A/B(OH)_3$ against the isoelectric pH (the points of intersection in fig. 3 *a*) as in fig. 4 *a*, curve I. It is interesting to note how closely this curve agrees, with respect to position and form, with the experimental curve in fig. 4 *b*, obtained by isoelectrically precipitating humic acid and aluminum hydroxide, and adapted from an earlier publication (MATTSON, 1931 a).

It should also be noted that the deflection of the isoelectric point is not only related to the molar ratio of acid to hydroxide but to their apparent dissociation constants as well. This again is best illustrated graphically. If instead of the acid H_3A we add to the hydroxide the acid H_3A', whose apparent dissociation constants are $k'_{a_1} = 10^{-7}$, $k'_{a_2} = 10^{-8}$ and $k'_{a_3} = 10^{-9}$, and plot the corresponding curves, we obtain the results shown in fig. 3 *b* and 4 *a*, curve II. It will be seen that the weaker acid H_3A' gives, with the hydroxide $B(OH)_3$, an isoelectric series, which covers a smaller range of pH than the series formed with the stronger acid, that is, the weaker acid deflects the isoelectric point less, and attains the limiting value more abruptly than the stronger acid. By extrapolation we see, that a sufficiently weak acid would not combine with the hydroxide, and not affect its isoelectric point. A stronger acid would produce the opposite effect, giving a greater deflection, and, therefore, a wider isoelectric series. The effect of the strenght of the hydroxide in combination with a given acid would be the same, a stronger hydroxide giving a wider isoelectric series than a weaker one.

With reference to the effect of acids of different strenght on the net capacity of the complex to bind base, and to exchange cations, an inspection of fig. 3 *a* and 3 *b* will show

that, at a given pH, not to far above the isoelectric points, e. g., at pH 7, the stronger acid produces the greatest effect: *The lower the isoelectric point the greater is the cation exchange capacity*. At very high pH, however, this difference vanishes, for even the weakest acid will bind as much base as the strongest at sufficiently high pH. Hence laterites bind as much, or more base than silicious colloids at high pH values.

The effect of the strenght of the hydroxide on the cation exchange will be the opposite to that of the acid. To illustrate this let us consider the interaction of the acid H_3A with a weaker hydroxide $B'(OH)_3$ having the apparent dissociation constants $k'_{b_1} = 10^{-9}$, $k'_{b_2} = 10^{-10}$ and $k'_{b_3} = 10^{-11}$. Its capacity to bind acid ($\Sigma y'$) is represented by the broken curve in fig. 3 *a*. An inspection of the figure shows (1) that the isoelectric points are lower in all cases, and (2) that the acidic residues, and, therefore, the power to bind base and exchange cations are greater. This agrees with the observed facts that the ferric complexes (silicates, humates and phosphates) have a lower isoelectric point and a greater cation exchange capacity than the aluminum complexes of corresponding composition (MATTSON, 1931 b).

We shall now complete the graphic presentation by plotting the Σx—y values of 1 mol of the hydroxide $B(OH)_3$ in combination with various proportions (0.1 to 8 mols) of the acid H_3A. Fig. 5 *a* shows the central portions of the titration or buffer curves thus obtained and which represent the net capacities of the different systems to bind acid (negative values) and base (positive values). The point at which a curve intersects the line corresponding to the zero position on the abscissa in the isoelectric point of the complex. Similar series of curves have been obtained by titrating isoelectrically precipitated silicates, phosphates and humates of aluminum and iron (MATTSON & HESTER, 1932).

For comparison with fig. 5 a, fig. 5 b, c and d are here reproduced. Fig. b shows the titration curves of two isoelectrically pecipitated and electrodialyzed alumino silicates

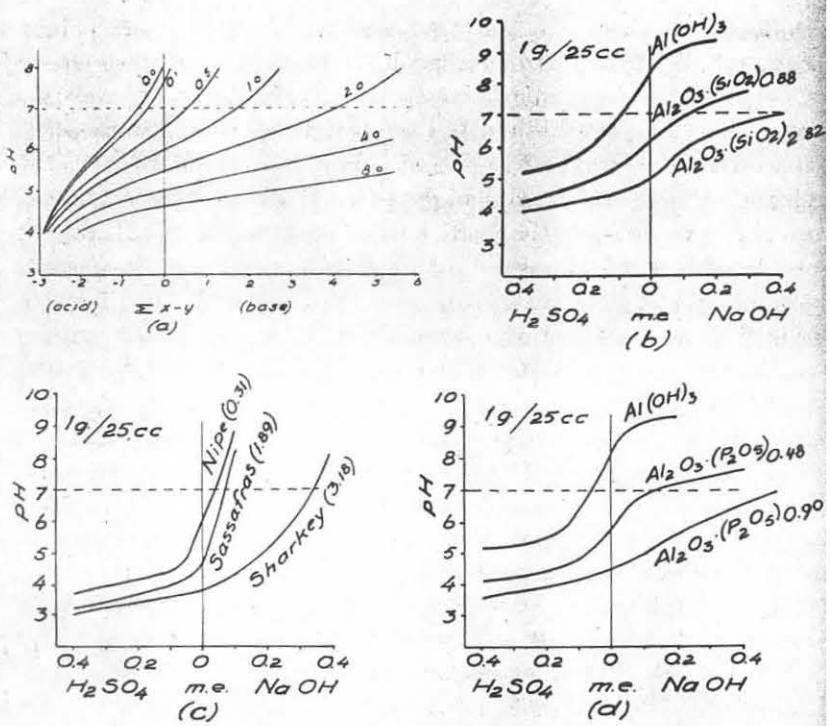


Fig. 5.

(*a*) The titration curves of systems containing 1 mol $B(OH)_3$ and 0.0 to 8 mols H_3A. (Comp. fig. 3 (*a*)).

(*b*), (*c*) and (*d*). The titration curves of isoelectrically precipitated aluminum hydroxide, silicates and phosphates and of three electrodialysed soils.

together with aluminum hydroxide, fig. d shows the titration curves of a corresponding series of phosphates, whereas fig. c shows the titration curves of three electrodialysed soils, namely, the Nipe laterite, the Sassafras loam (brown soil) and the Sharkey clay soil. The figures on the soil curves give the SiO_2/M_2O_3 ratio in the soil colloids. The slope of the curves depends, of course, upon the concentration of the colloid and upon the scale chosen. But the point of intersection with the zero line is determined, apart from the dilution effect, by the isoelectric point of the complex. It will be noted that

this point is lower the higher the acidoid/basoid ratio exactly as in the theoretical case.

In studying the amphoteric humates of aluminum and iron an anomali was encountered. It was found that the humate systems, having a high proportion of humic acid and therefore a low isoelectric point, possess a second isoelectric point at a still lower pH, and that systems having a very high proportion of humic acid remain anodic, having no isoelectric point, no matter how low the pH (MATTSON, 1931 a). There is no theoretical basis for this behavior in fig. 3. The functions x and y express the sum of true salt formation and dissociation, and the isoelectric point is defined as the point where the anionic and cationic dissociation of the complex are equal or where $\Sigma x - y = 0$. But dissociation is not alone responsible for the potential difference at the interface and the charge of the colloid. The charge may also be caused by an association with ions, and by an interaction with electrical dipoles. The fact is that inert substances in general charge themselves negative in water. This being the case, we must assume that all colloids dispersed in water possess a residue e of negative charge, apart from their ionization. An amphoteric colloid can therefore not be isoelectric before the dissociation of anions exceeds the dissociation of cations by an amount equal to e. In other words the isoelectric point will be at the pH where $y = x + e$ and not where $y = x$.

This would not alone explain the second isoelectric point at a lower pH, and the return of the complex to the anionic or negative condition, because a lowering of the pH will result in a greater ionization of the basic group, and a repression of the ionization of the acidic group, i. e., in an increase in y and a decrease in x. But since the pH is lowered by an acid (HCl) with which aluminum hydroxide forms a soluble salt, Al ions pass into solution, whereas the colloidal humic acid remains in the complex. The positive charge of the latter is thereby reduced until we get a second isoelectric point and finally, when e dominates, an anionic complex. There must

be a certain minimum of basic groups in the complex in order to render it electropositive or isoelectric, and since this minimum cannot be maintained at low pH, due to the solubility of the hydroxide, a complex with a high proportion of acidoid must remain anionic. This does not, however, prevent such a complex from reacting amphoterically: Soil colloids which have a high acidoid/basoid ratio, have no isoelectric point but react amphoterically, combining with anions as well as with cations. They are characterized by an equi-ionic point (MATTSON & GUSTAFSSON, 1935 b). This is defined as the pH at which the anions and cations of a salt are equally adsorbed by the complex and at which the salt produces neither exchange alkalinity nor exchange acidity.

Precipitates of soluble acids and colloidal hydroxides.

In the foregoing we have assumed that the interacting acid and hydrous oxide are themselves colloidal. It is then obvious that both components, no matter in what proportions they are added to the system, will quantitatively be precipitated in the isoelectric complex. Aluminum hydroxide and humic acid form such a system. In the experimental work referred to, the humic acid was completely precipitated at the isoelectric points. The experimental curve, relating the composition ratio to the isoelectric pH, shown in fig. 4 *b*, resembles therefore the theoretical curves in fig. 4 *a*, which express the total number of mols of H_3A per mol $B(OH)_3$, whether combined or uncombined.

But if the acid is soluble, it will only be the combined fraction which will be precipitated. The remainder will remain in solution. If the acid H_3A were a soluble acid, a part of it would remain in solution, even at the isoelectric point where the union between the acid and the hydroxide is a maximum (comp. fig. 3 *a*). Table 2 A gives the approximate, combined and uncombined mol fractions of H_3A at the isoelectric points

Table 2.

The combined and uncombined mol fractions of H_3A ($k_{a_1} = 10^{-5}$, $k_{a_2} = 10^{-6}$, $k_{a_3} = 10^{-7}$) at the isoelectric points when mixed, in the given proportions, with $B(OH)_3$ ($k_{b_1} = 10^{-7}$, $k_{b_2} = 10^{-8}$, $k_{b_3} = 10^{-9}$) as based on fig. 3 a, and the corresponding figures obtained by the isoelectric precipitation of different alumino phosphates and silicates.[1] A graphic presentation is given in fig. 6 *a*, 6 *b* and 7 *a*, 7 *b*.

(A)

Mols $B(OH)_3$ in mixture	Mols H_3A in mixture	Isoelectr. pH (approx.)	Mols H_3A combined (approx.)	Mols H_3A uncomb. (approx.)
1	0.1	7.55	0.09	0.01
1	0.5	6.55	0.33	0.17
1	1	6.0	0.50	0.50
1	2	5.45	0.67	1.33
1	4	5.0	0.80	3.20
1	8	4.6	0.88	7.12

(B)

Mols $AlCl_3$ in mixture	Mols Na_2HPO_4 in mixture	Isoelectr. pH	Mols PO_4 in precipitate	Mols PO_4 in solution	Composition of precipitate
5.00	2.495	6.45	2.410	0.085	$Al_2O_3 \cdot (P_2O_5)_{0.48}$
5.00	5.482	5.6	3.843	1.639	$Al_2O_3 \cdot (P_2O_5)_{0.77}$
4.96	10.156	4.9	4.252	5.904	$Al_2O_3 \cdot (P_2O_5)_{0.86}$

(C)

Mols $AlCl_3$ in mixture	Mols Na_2SiO_3 in mixture	Isoelectr. pH	Mols SiO_2 in precipitate	Mols SiO_2 in solution	Composition of precipitate
5.00	3.562	6.6	2.734	0.828	$Al_2O_3 \cdot (SiO_2)_{1.09}$
5.00	6.718	6.25	4.072	2.641	$Al_2O_3 \cdot (SiO_2)_{1.63}$
5.00	16.650	4.7	6.443	10.207	$Al_2O_3 \cdot (SiO_2)_{2.62}$
7.50	37.500	4.2	10.660	26.840	$Al_2O_3 \cdot (SiO_2)_{2.90}$

[1] The phosphate and silicate mixtures in total volumes of 2 500 cc.

of the different mixtures as based on fig. 3 *a*. We note that the uncombined fraction increases rapidly as the amount of added acid is increased, and as the isoelectric pH is decreased, and, conversely, that the combined fraction is proportionally much greater in low than i high concentrations of the acid. The relationship is shown graphically in fig. 6 *a*. The scattered figures along the curve represent the isoelectric points. We thus obtain an »adsorption» isotherm on a purely chemical basis.

Fig. 7 *a* shows (1) the total number of mols H_3A per mol $B(OH)_3$ in the mixture, and (2) the combined number of mols H_3A, each in relation to the isoelectric pH. If now the acid is soluble, and the uncombined fraction remains in solution, we would get isoelectric precipitates, whose composition is expressed by the lower curve, and not by the upper curve, which expresses the composition of the mixture. It will be noted that the lower curve runs asymptotic to a certain composition, in this case to $H_3A/B(OH)_3 = 1$, whereas the upper curve runs asymptotic to a certain pH. This means that the composition ratio, acid/hydroxide, in the precipitate is in one case (when the acid is soluble) limited and in the other case (acid colloidal) unlimited.

We shall now see that the theory here developed is in perfect agreement with the experimental results obtained in the isoelectric precipitation of systems containing soluble acids and colloidal hydroxides, such as the phosphates and silicates of aluminum and iron. Silicic acid behaves in the dilutions employed and when freshly prepared, as a soluble acid (Freundlich, 1922).

Table 2 B and C gives the composition of the mixtures (column 1 and 2), the isoelectric pH, the quantities of acid in the precipitate and in the solution after precipitation, and the composition of the isoelectric precipitates of the aluminum phosphate and silicate systems.

For a better comparision with the above described theoretical case the results have been plotted in a similar way in fig. 6 *b*

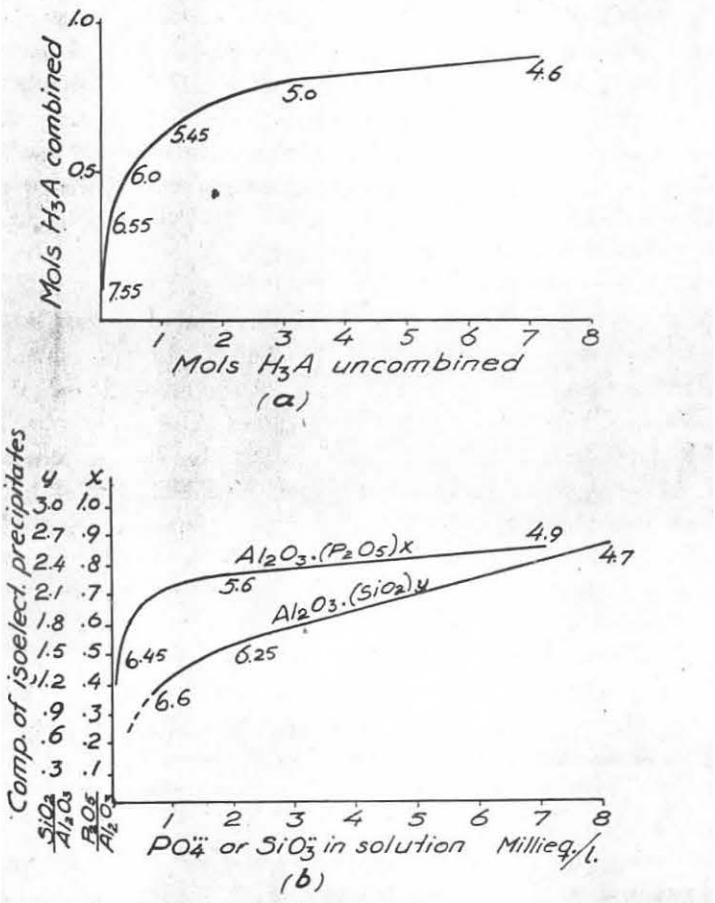


Fig. 6.

(*a*) The relationship between the (with $B(OH)_3$) combined and uncombined H_3A as based on fig. 3 *a*. (Comp. table 2 (A).) Scattered figures represent isoelectric points.

(*b*) The relationship between the combined and uncombined H_3PO_4 and H_2SiO_3 in various isoelectric alumino phosphate and silicate systems. (Comp. table 2 (B) and (C).)

and 7 *b*. We note in fig. 6 *b* that the hydroxide precipitates almost completely small amounts of silicic acid and, especially, phosphoric acid but that the higher isoelectric phos-

phates and silicates exist in equilibrium with ever increasing quantities of phosphoric and silicic acid in solution. The isoelectric composition in relation to the pH is shown in fig. 7 *b*. The composition of the precipitate does not follow the composition of the mixture as in the case of the humates (colloidal acid), but approaches a limiting value, which, for the

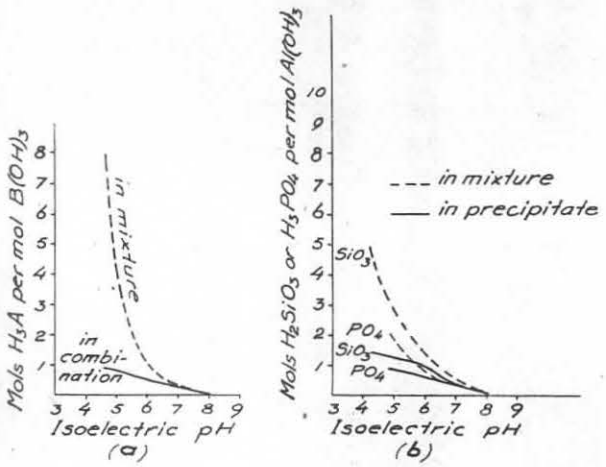


Fig. 7.

(*a*) The relationship between the ratio $H_3A/B(OH)_3$ in the mixture and in combination, and the isoelectric point as based on fig. 3 *a*. (Comp. table 2 (A).)

(*b*) The corresponding relationship in the isoelectric alumino phosphate and silicate systems.

phosphates, appears to be $PO_4/Al = 1$ and, for the silicates, $SiO_3/Al = 1.5$.

The fact that the isoelectric phosphates and silicates, especially the higher ones, exist in equilibrium with a certain amount of free acid in solution is of interest in relation to soil formation. It means that these and similar compounds are unstable even at their isoelectric point at which their stability is at a maximum. For if the free acid is removed by leaching or otherwise, a new equilibrium must be established. The acid lost by the solution will partially be replaced at the expence

of the complex, whose isoelectric point is thereby deflected to a higher pH. The process is best illustrated by stating that the composition and the isoelectric point will move from left to right in fig. 3.

Another result of the solubility of the acid, is that, when the basic constituent becomes ionized and soluble at pH below the isoelectric point, the whole complex will dissolve and vanish as a colloidal entity. There will not in this case (as in the case where the acid is colloidal) be formed a complex which is richer in acid and poorer in hydroxide, and which has a lower isoelectric point than the original complex. In other words, the composition and the isoelectric point cannot, in this type of colloid, move from right to left in fig. 3 by a mere leaching out of the ionized basic group, because the unionized but soluble acid will simultaneously be lost.

As far as the phosphates are concerned we have, of course, complete solubility of the acid constituent. But phosphoric acid represents such a small percentage of the soil, that its, practically, complete retention is, according to fig. 6 *b*, assured. It should be pointed out that the relatively large mol fraction of phosphoric and silicic acid which, according to table 2, remained in solution, becomes very much smaller in the soil, where the ratio of solution to the solid phase is several thousands times smaller than in the experiments.

Regarding the silicates, it must be remembered that the isoelectric precipitates were prepared in very dilute solutions by adding Na_2SiO_3 to $AlCl_3$. If, instead of the sodium salt, a silicic acid sol was used in the ratio of 14 mols SiO_2 to 1 mol Al_2O_3, a precipitate with the composition $Al_2O_3 \cdot (SiO_2)_{10.35}$ was formed (MATTSON, 1930). This precipitate had, like the higher humates, no isoelectric point, being anionic over the entire range of precipitation. Large amounts of free silicic acid were obviously here precipitated.

Silicic acid occupies evidently an intermediate position between a soluble and a colloidal acid. When freshly prepared in dilute solution it possesses a high diffusion coefficient, but

it quickly ages into a colloidal solution, whose stability is affected by several factors. Unlike other negative sols, it is sensitized by hydroxyl or possibly by silicate ions (FREUNDLICH, 1922). The sol is thus not coagulated by rather large concentrations of neutral salts, whereas small concentrations of the salt will suffice if a little alkali is added. The sol may also be coagulated by the addition of a fine powder as already observed by GRAHAM (1865).

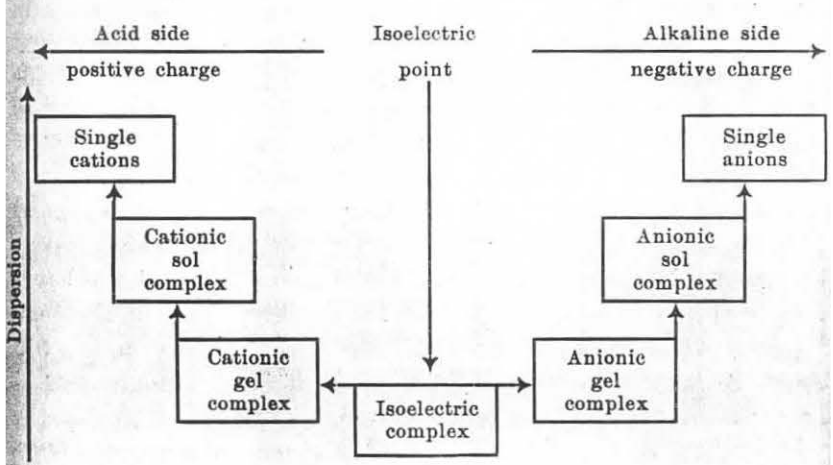
We know very little about how silicic acid interacts in the soil. It seems probable that, unionized, it exists and moves mainly in the colloidal condition. This believe is supported by several facts. Thus, if the basic group of the soil complex is ionized and dissolved by the addition of an acid, much less silica is dissolved than is set free by the decomposition of the silicate. The cation complex is associated with some silica, as it is with humic acid, but this is evidently the result of an incomplete hydrolysis. Similarly, in the A_2 horizon of the podzol profile, a complex is left behind, after the ionization and leaching of Al and Fe, which is richer in silica and has a lower isoelectric point than the original material. The process is apparently dominated by the isoelectric type of weathering. If unionized silica were soluble to any appreciable extent, podzolic weathering would lead to a complete solution, and the older soils in humid regions would long ago have lost their silica, and would today be highly lateritic. Isoelectric weathering is, obviously, only then fully realized when the acidic as well as the basic constituent of the complex are themselves colloidal in the unionized and uncombined condition.

In the foregoing we have discussed the theory of the interaction of colloidal hydroxides with soluble acids. The alternative case, i.e., the interaction of colloidal acids with soluble bases need not be considered, because all the basic hydrous oxides of the soil are insoluble. The interaction of soluble acids and bases leads to stoichiometric compounds. These play no important roll in relation to the amphoteric behavior

of the soil colloidal complex beyond the exchange reactions their ions enter into with the latter.

The anionic and cationic gel and sol complex. Theoretical.

We shall now introduce a new conception, which, in our opinion, will not only be useful but absolutely essential for an understanding of the intricate processes of soil formation. We have already distinguished between three states of aggregation, namely, (1) the gel state, (2) the sol state, and (3) the state of ultimate solution of single ions. But, in the case of amphoteric colloids, the series repeats itself on either side of the isoelectric point, with the difference that one series is electronegative or anionic and the other is electropositive or cationic. The material making up the soil colloidal complex may, therefore, exist in seven distinct forms according to the following scheme:



Between these forms we meet with every degree of transition. At the isoelectric point the positive and negative charges are balanced. We do not believe that the charges are equal to

zero at this point, because many facts point to a »zwitterionic» condition of the soil complex (MATTSON & GUSTAFSSON, 1935 a). As the pH of the medium is lowered or raised the gel complex becomes increasingly cationic or anionic, respectively, and passes, at a certain degree of charge, into the sol condition. But the complex becomes not only more highly dispersed; it also undergoes a hydrolytic decomposition.

Let us illustrate this by referring to table 1 (D) and to fig. 2 *d*. Here we have equivalent quantities of H_3A and $B(OH)_3$. At the point I (= pH 6) the union between A and B is a maximum (or 50 %). This is the isoelectric point. Suppose now that the pH is lowered to about 4.55 by the addition of a strong acid with which the hydroxide forms an ionized and soluble compound. The hydroxide is here about 90 % combined, whereas the acid H_3A is about 90 % uncombined, being combined with the hydroxide to the extent of only 10 %. The cationic sol complex, which, because of the strong positive charge and the resulting high degree of hydration, splits off from the gel complex, is therefore richer in B and poorer in A than the original complex, isoelectric at pH 6. The liberated acid, H_3A, will, if soluble, pass into solution or it will, if insoluble, remain in the gel, which thereby becomes enriched in this constituent, resulting in a lowering of its isoelectric point (isoelectric weathering). The cationic sol complex will have a higher isoelectric point than the original complex, and this point will be higher the lower the pH at which it was ionized and split off from the gel complex, because the lower the pH the more complete will be the hydrolysis of the complex. At sufficiently low pH the cationic sol complex will resolve itself into single B^{+++} ions.

It must be pointed out that the above holds only for the case that the acid, which is added to lower the pH of the system, is an acid, which forms an ionized compound with $B(OH)_3$. If an acid is added, which resembles the acid H_3A in so far that it forms a practically unionized and insoluble compound with $B(OH)_3$, then it is obvious that the complex

will not become cationic, and will not disperse, even though the pH be lowered. The effect would then be the same as when the proportion of H_3A is increased as illustrated in fig. 3 *a*. The isoelectric point would be lowered, and it would, therefore, require a still lower pH to ionize the basic group of the complex. This explains the lowering of the isoelectric point of a soil by the addition of H_3PO_4, or even H_2SO_4, as compared to HCl (MATTSON, 1931 c).

The effect of an increase in pH will be the opposite, for then it will be the acidic group which will be ionized, forming an anionic sol complex, which is richer in A and poorer in B than the original complex, whereas the latter becomes correspondingly richer in B. (Since $B(OH)_3$ itself is amphoteric it will of course ionize and disperse at sufficiently high pH.)

We now come to one of the most important principles of soil formation, namely, the mutual interactions of the soil complexes. To illustrate this let us assume that the cationic sol complex, which is split off from the parent gel complex at pH 4.55, has the composition of 0.1 mol H_3A to 1 mol $B(OH)_3$. The isoelectric point would, according to fig. 3 *a*, be at pH 7.55. The complex would act as a base and bind acid up to this pH, as indicated by the negative Σ x—y values in table 1 (B). If the pH is increased to 7.55, the cationic sol complex, which we shall designate by the formula $H \cdot a \cdot b^+$, would become isoelectric as follows:

$$\underset{\text{cationic sol complex}}{H \cdot a \cdot b^+} + OH^- \rightarrow \underset{\text{isoelectric gel complex}}{H \cdot a \cdot b \cdot OH} \qquad (1)$$

But suppose that, during the upward climb of the pH, the cationic sol complex encounters a complex, which has a lower isoelectric point such as, for example, the original parent gel complex isoelectric at pH 6. This complex becomes anionic at a pH above 6, where it begins to act as an acid and to bind base, as indicated by the positive Σ x—y values in table 1 (D). Within the range of pH from 6 to 7.55, one complex

will act as acid and the other will act as base. The obvious result of this is a chemical interaction resulting in a new complex, whose isoelectric point will be determined by the proportions of the interacting complexes, but wich must be somewhere between pH 6.0 and 7.55. If we designate the anionic gel complex by the formula $^{-}A \cdot B \cdot OH$ we can express the interaction by the following equation:

$$H \cdot a \cdot b^{+} + {}^{-}A \cdot B \cdot OH \rightarrow H \cdot a \cdot b \cdot A \cdot B \cdot OH \qquad (2)$$

cationic sol complex	anionic gel complex	isoelectric gel complex

The important difference between the two equations is that in equation (1) the cationic sol complex is precipitated at its own isoelectric point by combining with OH ions, whereas in equation (2) it is isoelectrically precipitated at a lower pH by uniting with an anionic complex. That such mutual interactions between soil colloids actually occur was shown in a previous paper (Mattson & Gustafsson, 1935 a).

EXPERIMENTAL PART.

The gel and the sol complex.

In a previous work (Mattson & Nilsson, 1935) we studied the composition and amphoteric properties of the sol complex obtained in the extracts (pH 3.2 to 3.7) from a series of mixtures of a mineral soil with various proportions of humus. Since only one extract was prepared from each mixture, we decided to continue the work by studying each mixture in series of varying pH. We are here presenting the result of this work. The materials used and the method employed were as follows:

Samples of 200 g. of the B_2 horizon of the previously described Häggbygget podzol (Mattson & Gustafsson 1935 a)

were shaken for 15 hours in a total volume of 2 liters in 20 × 30 cm hot water bags, together with the following quantities of humus from the H-layer of the same profile:

Series I, no humus; series II, 12.5 g.; series III, 25 g.; series IV, 50 g., and series V, 100 g. humus.

Each series consisted of eight extractions, which differed from one another in the amount of NaOH or HCl added to cover a range of pH from about 3 to 7. In addition to the soil + humus series, a series containing 25 g. humus alone was included. In order to have a fairly uniform concentration of electrolyte in each mixture, NaCl was added in such an amount that the sum NaCl + NaOH or NaCl + HCl was never less than 20 milliequivalents in 2 liter. The shaking was done 7 hours the first day, 7 hours the second and 1 hour the third day. The rubber bags proved excellent for this work.

The extracts were filtered through a triple layer of 11 cm No 00 Berzelius filters in Büchner funnels. The edges of the wet papers were sealed on to the porcelain by adding some melted paraffin and rotating the inclined funnel until the paraffin lost its fluidity. The funnel was then placed in the suction flask and the filter was sucked tight to the bottom until the paraffin was quite hard. After pouring back the first portion of the filtrate, which sometimes was slightly turbid, we were thus able to obtain clear extracts.

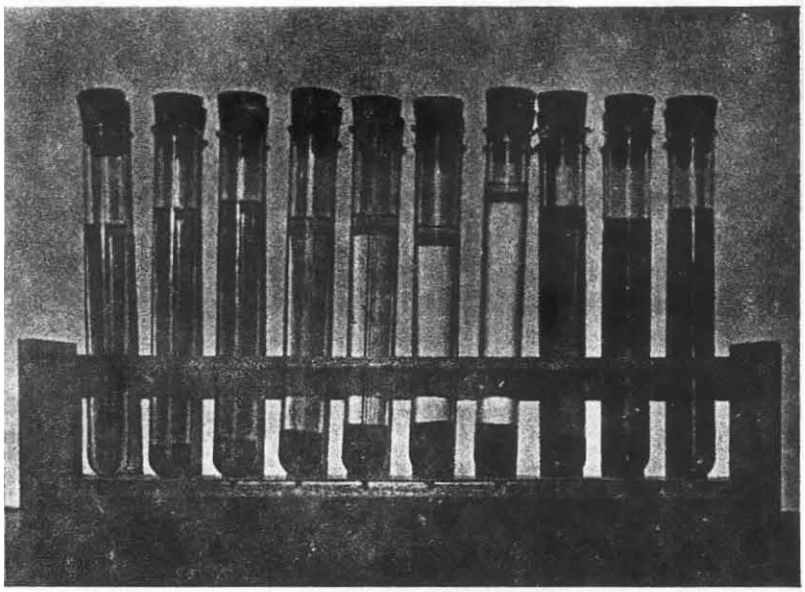
The extracts were examined as follows:

(1) *The color:* The extracts were nearly colorless in the neighborhood of the isoelectric point of the mixture. At higher and lower pH the color became yellow and then brown.

(2) *The pH:* This was determined by the quinhydrone method.

(3) *Flocculation and cataphorese:* 50 cc portions of an extract are placed in a series of large test tubes, usually about 10 to 12 tubes. In a preliminary test the quantity of NaOH or HCl required to produce the most rapid flocculation, if any, is determined. This quantity is then added to one of the tubes

in the middle of the series. In one direction this quantity is progressively decreased until no flocculation is observed, and in the other direction it is increased until the sol again fails to flocculate or until a certain amount has been added. The following day 20 cc of the liquid in each tube is withdrawn for pH determination. The precipitate is then suspended in



The isoelectric precipitation of the cationic sol complex (see table page 31).

the remaining liquid by inverting the tubes, and the cataphoresis is determined by the ultramicroscopic method as previously described (MATTSON, 1928). The isoelectric point is found by interpolation, when not directly observed (comp. fig. 8).

One such series consisting of 10 tubes is shown in the above photograph. The data obtained for this series was, from left to right, as follows:

No	1	2	3	4	5	6	7	8	9	10
Flocculation	0	x	xx	xxx	xxxx	xxxx	xxxx	xx	x	0
pH	3.03	3.90	4.64	4.85	5.20	5.59	6.12	6.60	7.10	8.04
μ/sec. 1 volt/cm.	—	+1.96	+1.88	+0.86	+0.24	±0.0	−0.26	−1.03	−2.12	—

The flocculation is designated by X's, one X signifying slight, and four X's complete flocculation. The electrical migration of the particles has been reduced to μ per second, in a potential gradient of 1 volt per cm. It will be noted that the sol flocculated completely in only three of the tubes, at pH 5.20, 5.59 and 6.12, and that the floc was isoelectric at pH 5.59, i. e., in the sixth tube from the left.

(4) *Organic matter:* This is put equal to the loss on ignition after 16 % of the weight of silica and sesquioxides, assumed as water lost by the inorganic gels, is subtracted. It was determined by evaporating 50 cc of the extract, drying at 105° C, and igniting at dull redness in the electric furnace.

(5) *Silica and sesquioxides:* These were determined in the ignited ash in the usual manner. The results are shown in table 3 and in fig. 8 to 14.

The results of the experiment, which agree in general with the theory outlined, are as follows:

1. There is a minimum in the amount of material dispersed at a pH which corresponds to the isoelectric point of the gel complex formed in the mixture. The B_2 soil material is rich in sesquioxides and has, therefore, a relatively high isoelectric point. The addition of humus suppresses the cationic ionization of the complex, thereby lowering the isoelectric point, together with the point of maximum stability. This is clearly illustrated in fig, 9, 10 and 11.[1]

[1] For the sake of clearness only four of the series are included in the figures.

Table 3.

The composition and isoelectric point of the sol complex, extracted at different pH from different mixtures of soil and humus. 200 g. soil in 2 liters.

I. *No humus.*

M. e. added	NaOH:			HCl:				
	10	4	0.0	2.5	5	10	20	40
pH of extract . . .	6.89	5.29	4.72	4.40	4.04	3.84	3.41	3.13
Isoelectric pH . . .	no floc	no floc	no floc	6.42	6.75	7.30	7.10	6.94
M. e. NaOH required[1]	—	—	—	2.0	4.5	9.4	19.2	38.6
Organic matter g. . .	.526	.153	.073	.124	.152	.221	.364	.888
SiO_2 » . .	.0088	.0080	.0032	.0048	.0067	.0134	.0244	.0496
Al_2O_3 » . .	.0456	.0251	.0224	.0594	.1088	.1800	.3527	.6668
Fe_2O_3 » . .	.0208	.0062	.0016	.0008	.0028	.0040	.0045	.0172
G.org.m./M.mol M_2O_3	.92	.54	.32	.21	.14	.12	.11	.13
SiO_2/M_2O_3	.25	.47	.28	.14	.10	.12	.11	.12

II. *12.5 gram humus.*

M. e. added	NaOH:			HCl:				
	15	6	0.0	2.5	5	10	20	40
pH of extract . . .	6.97	5.65	4.75	4.31	3.99	3.62	3.33	2.95
Isoelectric pH . . .	no floc	no floc	no floc	no floc	5.55	6.40	6.70	7.00
M. e. NaOH required[1]	—	—	—	—	2.6	7.3	17.2	36.0
Organic matter g. . .	.686	.287	.152	.205	.195	.280	.514	.852
SiO_2 » . .	.0084	.0116	.0048	.0076	.0108	.0176	.0272	.0708
Al_2O_3 » . .	.0348	.0192	.0196	.0452	.1038	.1604	.3111	.6582
Fe_2O_3 » . .	.0136	.0048	.0000	.0008	.0030	.0032	.0037	.0168
G.org.m./M.mol M_2O_3	1.61	1.32	.80	.46	.19	.18	.17	.13
SiO_2/M_2O_3	.33	.38	.41	.28	.17	.18	.15	.18

[1] To render the complex isoelectric.

III. *25 gram humus.*

M. e. added	NaOH:			HCl:				
	20	8	0.0	2.5	5	10	20	40
pH of extract . . .	6.89	5.51	4.60	4.31	3.98	3.70	3.35	2.98
Isoelectric pH . . .	anionic	no floc	no floc	no floc	4.75	5.61	6.30	6.32
M. e. NaOH required[1]	—	—	—	—	2.0	4.3	14.0	33.3
Organic matter g. . .	.972	.448	.226	.233	.308	.311	.526	1.186
SiO_2 » . .	.0168	.0196	.0100	.0104	.0236	.0328	.0328	.0624
Al_2O_3 » . .	.0509	.0268	.0191	.0232	.0369	.1080	.2788	.6267
Fe_2O_3 » . .	.0179	.0064	.0009	.0009	.0031	.0036	.0036	.0173
G. org. m./M. mol M_2O_3	1.60	1.48	1.17	1.00	.81	.29	.19	.19
SiO_2/M_2O_3	.46	1.07	.86	.74	.63	.50	.20	.17

IV. *50 gram humus.*

M. e. added	NaOH:			HCl:				
	30	12	0.0	2.5	5	10	20	40
pH of extract . . .	6.87	5.88	4.29	4.31	3.99	3.69	3.31	2.92
Isoelectric pH . . .	anionic	no floc	no floc	no floc	no floc	4.63	5.98	6.06
M. e. NaOH required[1]	—	—	—	—	—	1.8	10.7	29.8
Organic matter g. . .	1.464	.688	.382	.380	.380	.448	.676	1.145
SiO_2 » . .	.0240	.0232	.0148	.0176	.0240	.0332	.0376	.0664
Al_2O_3 » . .	.0594	.0348	.0231	.0232	.0288	.0841	.2052	.5512
Fe_2O_3 » . .	.0198	.0080	0009	.0012	.0032	.0031	.0032	.0160
G. org. m./M. mol M_2O_3	2.08	1.77	1.65	1.62	1.26	.53	.33	.21
SiO_2/M_2O_3	.56	.99	1.06	1.24	1.32	.65	.31	.20

[1] To render the complex isoelectric.

V. *100 gram humus.*

M. e. added	NaOH:			HCl:				
	40	20	0.0	2.5	5	10	20	40
pH of extract . . .	6.80	5.28	4.08	3.90	3.75	3.58	3.31	2.98
Isoelectric pH . . .	anionic	anionic	no floc	no floc	no floc	no floc	4.87	5.60
M. e. NaOH required[1]	—	—	—	—	—	—	4.0	22.4
Organic matter g. . .	2.105	1.289	.777	.672	.698	.704	.881	1.864
SiO_2 » . .	.0390	.0372	.0220	.0312	.0304	.0372	.0456	.0692
Al_2O_3 » . .	.0890	.0624	.0248	.0290	.0410	.0589	.1241	.4117
Fe_2O_3 » . .	.0240	.0124	.0012	.0010	.0026	.0017	.0019	.0115
G. org. m./M. mol M_2O_3	2.06	1.87	2.10	2.32	1.67	1.31	.72	.33
SiO_2/M_2O_3	.63	.89	1.45	1.79	1.21	1.14	.62	.28

2. On the acid side of the points of minima the sol complex is cationic, being isoelectrically precipitated by the addition of alkali (comp. fig. 8). The absolute amount of acidic as well as basic material dispersed, increases progressively as the pH is lowered, but the proportion of basic material becomes greater, and the isoelectric point of the sol complex becomes higher, the lower the pH of the extract. This is because the hydrolysis is more complete the lower the pH, resulting in a cationic sol complex, in which relatively little humic and silicic acid remain associated. This is shown in the table by the ratios of organic matter and of silica to sesquioxides.

3. At pH above the points of minima the sol complex is anionic, but is incompletely precipitated by HCl, and only in the more concentrated, dark colored extracts obtained at high pH. The precipitation was more complete in the presence of Ca, but the complex remained electronegative throughout the usual range of isoelectric precipitation; there was no isoelectric point, the proportion of humus being too high (comp. the aforementioned anomali).

[1] To render the complex isoelectric.

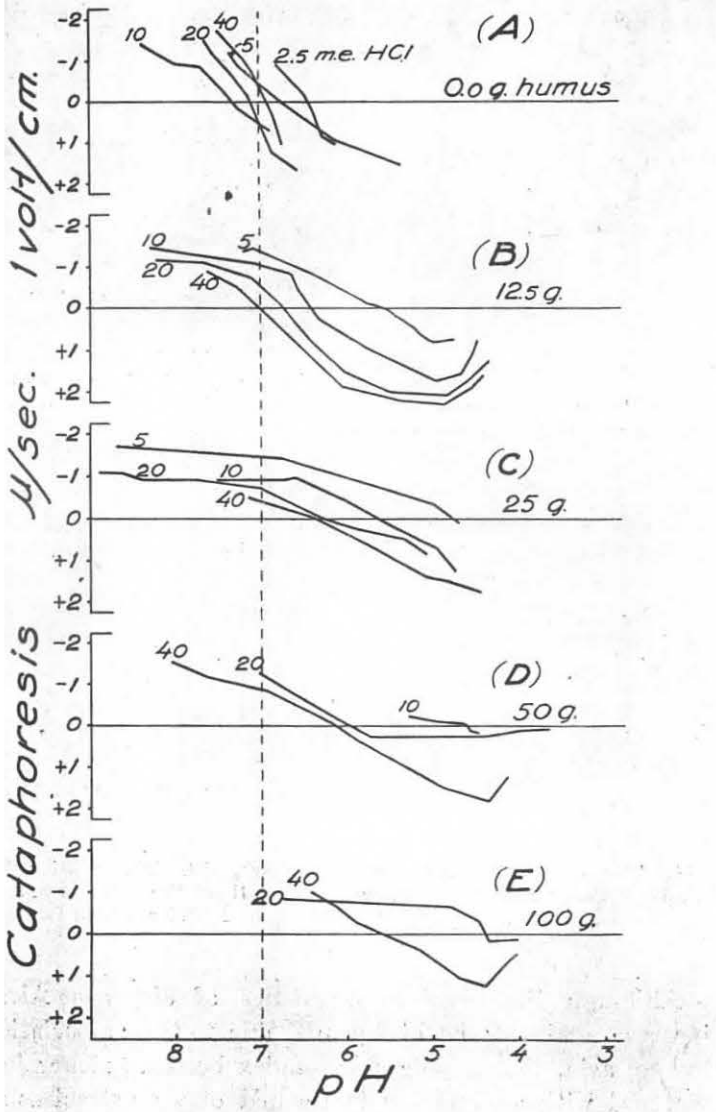


Fig. 8. The cataphoresis and isoelectric point of the extracted complex in relation to the acidity (m. e. HCl) and amount of humus added to 200 grams of soil.

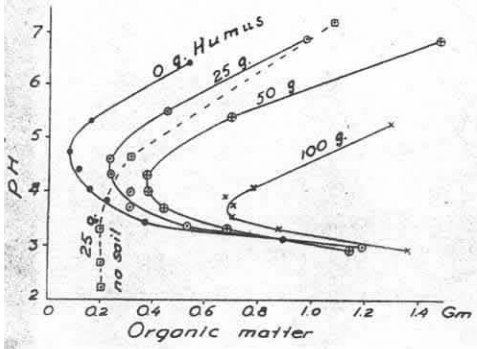


Fig. 9. The relation between the pH and organic matter in the extracts. The figures on the curves give the amount humus added to 200 grams of soil.

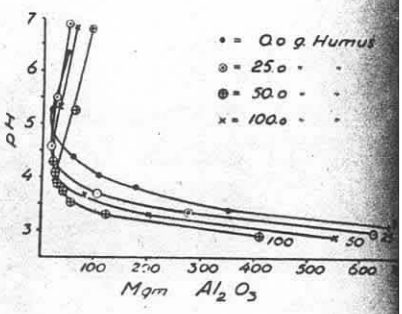


Fig. 10. The relation between the pH and Al_2O_3 in the extracts of the different series.

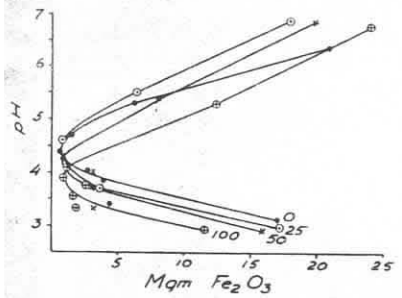


Fig. 11. The relation between the pH and Fe_2O_3 in the extracts of the different series.

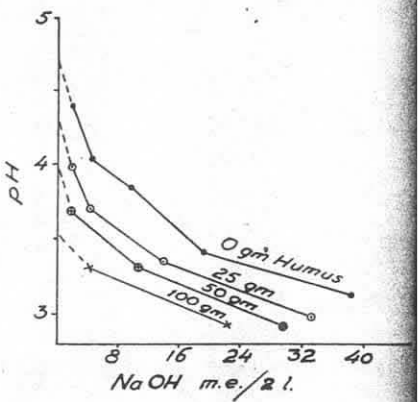


Fig. 12. The relation between the pH of the extracts and the amount of NaOH required for the isoelectric precipitation.

Although the absolute quantities of dispersed Al and Fe increase again at the higher pH, due to their association with humic acid, the anionic sol complex becomes richer in acidic material with an increase in the pH of the extract as a result of a progressive hydrolysis.

To sum up points 1, 2 and 3 we find that the soil complex is most stable at its isoelectric point, that there is an absolute in-

crease in the acidic and basic material dispersed on either side of this point, but that on the acid side the sol complex, which is

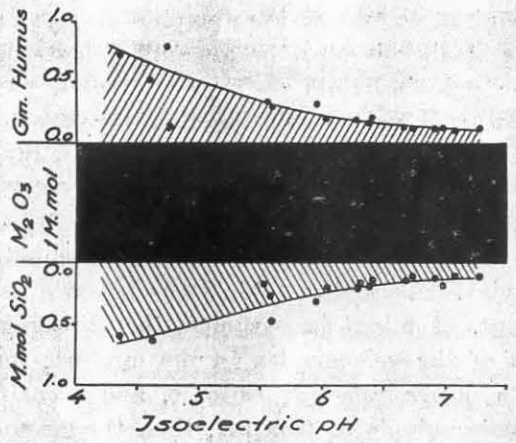


Fig. 13. The relation between the isoelectric pH and the composition of the extracts expressed in millimols silica and grams organic matter (humus) per millimol sesquioxides.

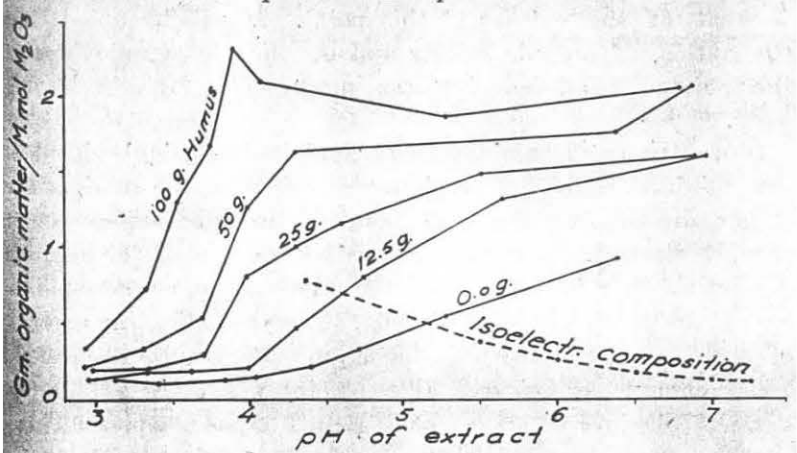


Fig. 14. The relation between the ratio of organic matter to sesquioxides and the pH of the extracts. The broken line shows the isoelectric composition (comp. fig. 13).

cationic, becomes progressively richer in basic material whereas on the alkaline side the sol complex, which is anionic, becomes progressively richer in acidic material This is all in complete agreement with the theory of isoelectric weathering.

The nearer the isoelectric pH of the cationic sol complex approaches the pH of the extract, the smaller is the amount of alkali required to render the complex isoelectric (comp. fig. 12), and the smaller is also the amount of material dispersed, whereas the acidoid/basoid ratio grows larger. At the point where the two pH values coincide there is no alkali required and there can, of course, be no isoelectrically precipitable quantities of the amphoteric complex in the extract, because, being isoelectric in the mixture, it was never dispersed beyond a certain amount representing, perhaps, the »solubility product» of the complex. As to the acidoid/basoid ratio in the extract at this point, it might be assumed, that this represents the composition of the gel complex in the mixture, for if a complex with a lower ratio is cationic, and a complex with a higher ratio is anionic at this pH, then the gel complex must here, where it is neither anionic nor cationic, not only be isoelectric but must also have a composition which corresponds to that of the extract at this point. It will be noted that the ratios of organic matter and of silica to sesquioxides at the points of minima increase progressively from system I to V.

Since the extracts obtained at, and in the neighborhood of the minima yield no precipitate, and since the minima are rather diffuse, the isoelectric point of the gel complex is not sharply defined. But apart from the position of the minima we get another index in regard to the position of these points by extrapolating the curves in fig. 12, representing the amount of alkali required to render the cationic sol complex isoelectric. This amount equals zero at the point where the pH of the extract coincides with the isoelectric pH of the complex. These curves point therefore like fingers to the isoelectric pH of the respective systems. The isoelectric point of the gel complex in the different systems may thus be estimated to lie between, let us say, pH 3.5 and 4.8. This agrees well with the amphoteric behavior of the two components as previously reported (Mattson & Gustafsson, 1935 a).

The fact that the minima for the different constituents, humus, Al_2O_3 and Fe_2O_3, do not agree so well need not surprise us. The amphoteric complex can, as a unit aggregate, have only one isoelectric point, but it must be remembered that it has a composite make-up, possessing a mosaic of acidic and basic groups, each ionizing according to its own activity, without regard to the isoelectric point of the aggregate, and only collectivitely determining the position of this point.

In regard to the behavior of the various constituents: organic matter, silica, and aluminium and iron oxides, the following should be noted.

Organic matter. The functions of the humus are as follows:

1. It lowers the isoelectric point of the complex (comp. the position of the curves in fig. 8 and the minima in fig. 9).

2. It suppresses the solubility of Al and Fe to a lower pH (comp. lower sections of curves in fig. 10 and 11).

3. It carries Al and Fe in dispersion, in the form of an anionic complex, at higher pH (comp. upper sections of curves in fig. 10 and 11).

4. Its nature and its degree of humification affect the above functions. Thus the finely divided organic matter, (F_0), of the ground vegetation from the same podzol profile (Vaccinium type), caused a greater solution of Al and Fe at low pH than the humus (H). Electrodialysis of the F_0 material yielded 30.8 milliequivalents bases and 17.9 m.e. dialyseable acids per 100 gram, whereas the H material yielded only 8.4 and 1.86 m.e. respectively. We must conclude that it is the colloidal humic acids which fix Al and Fe, and protect them from solution at low pH, whereas it is the diffusible acids, which are responsible for the ionization and dispersion of the bases. The interaction of the various forms of organic matter with the mineral complex is an important problem, which deserves a thorough investigation.

It will be noted that the lower sections of the curves in fig. 9 are bundled together. The system to which no humus

was added yields about as much cationically dispersed humus as the other systems. An investigation recently carried out by Dr. Boratyński in our laboraty has shown that the, cationically, dispersed humus practically all comes from the B_2 complex and not from the added humus. This points to a fundamental difference between soil humus and peat humus. The compound formed during the shaking between the soil complex and the added humus is easely hydrolysed, so that very little of this humus is carried in dispersion by Al and Fe, whereas the soil humus precipitated in nature, in the B_2 horizon, is firmly bound. This is again reflected by the upper section of the O-curves in fig. 10 and 11, which tend to intersect the other curves. This means that the Al and, especially, the Fe is more firmly bound to the soil humus than to the added humus. The former carries relatively more Fe and Al in dispersion than the latter. The difference between the two combinations seems to be the same as the difference between the synthetic and natural alumino-silicates. The question will be discussed in a forthcoming publication.

Aluminum and iron. The functions of Al and Fe may be summarized as follow:

1. They elevate the isoelectric point of the complex.

2. They carry humus and silica in dispersion in the form of a cationic complex. This is strikingly shown in fig. 9. The broken curve represents a system containing 25 gram humus but no soil. We note that there is here no appreciable increase in the dispersion of humus at low pH. The slight increase might be due to the effect of the small amounts of sesquioxide present, or it might be due to the amphoteric nature of the humus itself.

3. The difference in behavior between Al and Fe is of fundamental importance. We know from previous work (Mattson 1931 b) that the ferric compounds have a lower isoelectric point than the aluminum compounds of corresponding composition. Iron required, accordingly, a lower pH for its ca-

tionic dispersion, and appeared, in appreciable amounts, only in the most acidic extracts, around a pH of 3, whereas Al began to increase at, from one half to one pH unit higher. At the minima there are mere traces of iron present, the quantities being about 20 times smaller than those of aluminum. (Note the difference in scale in fig. 10 and 11.) This all points to a greater stability of the ferric humates. This conclusion is supported by the reversed order of dispersibility in the anionic complex, in which the iron shows a relatively greater increase than aluminum. (Comp. the upper sections of the curves in fig. 10 and 11.) It should be mentioned that ferrous humates have higher isoelectric points even than those of aluminum. Ferrous iron is therefore cationically dispersed at still higher pH, but this question will be discussed in connection with the aforementioned work of Boratyński.

Silicic acid. The functions of silicic acid is obscured by those of humus, which is present in far greater amounts. It can however be said that, like humus, it lowers the isoelectric point of the complex and suppresses the solubility of Al and Fe to a lower pH.

On the basis of other experiments, it does not seem to carry Al and Fe in dispersion at pH above the isoelectric point of the gel complex, at least not to any appreciable extent.

Another deviation is that, on the anionic side, there seems to be a maximum, the silica showing a tendency to decrease at the highest pH. This would be in harmony with the known peculiarity of silica sol to form a gel or to precipitate most easely at a pH slightly above the neutral point.

In order to illustrate what has been said in the last two paragraphs, an older, but unpublished, experiment with electrodialysed Ancylus clay will here be included. Samples of 25 grams clay were shaken for 36 hours in 500 cc of water, in the presence of HCl, NaOH, $Ca(OH)_2$ and MgO. The suspensions were then filtered through Pasteur-Chamberland filters, and 400 cc of the filtrate were analysed, with the result shown in table 4.

Table 4.

Silica and sesquioxides dissolved at various pH from 20 grams electrodialysed Ancylus clay.

M. e. added		pH	SiO_2 g.	Al_2O_3 g.	Fe_2O_3 g.	$\frac{SiO_2}{M_2O_3}$	$\frac{Al_2O_3}{Fe_2O_3}$
HCl	4.0	3.4	.0872	.0865	.0041	1.61	14.0
»	2.0	3.85	.0281	.0141	.0022	3.06	10.1
»	1.0	4.58	.0246	.0082	.0014	10.20	3.4
»	0.0	7.3	.0224	none	none		
NaOH	2.0	7.7	.0165	»	»		
»	4.0	7.8	.0134	»	»		
»	8.0	>9.6	.0197	trace			
$Ca(OH)_2$	2.0	7.4	.0212	none	»		
»	4.0	7.5	.0155	»	»		
»	8.0	8.0	.0085	»	»		
MgO	2.0	7.4	.0197	»	»		
»	4.0	7.7	.0110	»	»		
»	8.0	8.1	.0094	»	»		

The following points are of interest in connection with the present investigation:

1. Silica has a minimum somewhere above pH 8.
2. The solubility of silica does not seem to be markedly influenced by the nature of the base.
3. No Al and Fe is carried in solution by silica.
4. Silica is carried in solution by the sesquioxides, resulting in an apparent increase in the solubility of silica with a decrease in pH, but
5. the SiO_2/M_2O_3 ratio decreases rapidly with a decrease in pH. Therefore,
6. since the loss of silica dominates above a certain pH, and the loss of sesquioxides dominates below this pH, leading to an enrichment of the soil in sesquioxides in the first case,

and an enrichment in silica in the second case, we get an isoelectric weathering in the case of the silicate gel complex as in the case of the humate gel complex.

7. The Al_2O_3/Fe_2O_3 ratio increases with a decrease in pH. This means that Fe is relatively more soluble than Al at the higher pH. This we ascribe to the ferrous form of iron in this case, where we are dealing with a slightly weathered glacial clay. In podzolization iron is the first to become mobile (MUIR). Where we have ferrous iron this must be so, because the ferrous compounds have a higher isoelectric point than the corresponding compounds of Al and Ferric iron, and must therefore be the first to become cationically dispersed.

8. It is interesting to note that the glacial clay, from which 26 milliequivalents of base per 100 gram had been removed by electrodialysis, yielded an extract with a pH of 7.3, after 36 hours of shaking in pure water. Immediately after the electrodialysis the clay had a pH of 4.2. This »rock flour» will not long remain »unsaturated». It mobilizes new capital by drawing upon the principal, stored up in the vaults of the crystal lattices.

In fig. 13 we have graphically represented the composition of the isoelectric precipitates in relation to the isoelectric pH. The points are a little scattered but the increase in the acidoid/basoid ratio with a lowering of the isoelectric pH is clear enough. It must be remembered that these systems are more complex than the corresponding systems of »pure» humates and silicates represented in fig. 4 b and 7 b respectively. There is here other acidic and basic constituents than humus, silica and sesquioxides. Among the other materials present, phosphoric acid, titanium, manganese and ferrous iron might be mentioned. These all affect the isoelectric point. Then it must be pointed out that all the errors of the different procedures are here brought together. Chief among these are the errors envolved in cataphoresis. These are generally large and due to various causes. Then the composition of the extract might vary considerably, due to variations in the

permeability of the filters, as affected by the differents mixtures. Some filtered slowly, others more or less rapidly.

In fig. 14 we have plotted the humus/sesquioxide ratio in the extracts of the various series against the pH of the extracts. We have then inserted the upper curve in fig. 13 representing the isoelectric composition with respect to the same ratio (broken line). The points at which this curve intersects, or would intersect if extrapolated, the other curves correspond to the minima in fig. 9, and represent the isoelectric points of the gel complex in the different mixtures.

The curve is also a dividing line between the cationic and anionic sol complex. All points on the other five curves, which lie below this curve are on the acid side of the isoelectric point of the gel complex. The sol complex is therefore here cationic. The isoelectric point of any cationic sol complex is found by drawing a horizontal line to the right until it meets the broken line. All points which lie above the intersecting curve are on the »alkaline» side of the isoelectric point of the gel complex. The sol complex is therefore here anionic. The isoelectric point of an anionic sol complex is found by drawing a horizontal line to the left until it meets the broken line. This is however possible only within certain limits, because, according to the aforementioned anomali, a humate complex, whose proportion of humus exceeds a certain value, remains anionic even at low pH. The intersecting curve does therefore not continue indefinitely to the left.

The roll of the sol complex in soil formation.

If we calculate the molar ratios of silica to sesquioxides in the lithosphere, on the basis of the data supplied by Clarke (1920 p. 31) we get:

$$SiO_2/Al_2O_3 = 5.44 \text{ and } SiO_2/(Al_2O_3 + Fe_2O_3) = 4.27.$$

The ratios are for the silicate silica only, the 12 percent assumed to be quartz being subtracted, and FeO is calculated as Fe_2O_3.

We note that the ratios are very high. The isoelectric point of the gel complex, which is formed from the products of hydrolysis of the igneous rocks, must, therefore, be very low. This is especially true in the case of the soil where the gel complex contains humus in addition to silica as a dominantly acidic constituent. Since the lithosphere contains large quantities of the strong bases (there are 1.45 mols of CaO, MgO, K_2O and Na_2O per mol sesquioxides), which become liberated, we would expect the pH of the soil to stay above the isoelectric point of such a complex. This is also, normally, the case, except under special conditions, such as those leading to the formation of large quantities of organic and inorganic acids, to be discussed below.

A pH above the isoelectric point of the gel complex will give rise to a sol complex, which is anionic and, therefore, richer in acidoids than the parent gel, whereas the latter will become richer in basoids, and increase its isoelectric pH as the leaching proceeds. This must continue until the latter pH and the pH of the soil coincide. At this point the dispersed material has the same acidoid/basoid ratio as the parent gel complex. The position of this point will, to a large extent, depend on the magnitude of the humic constituent, which is maintained in the gel complex, and which is governed by various factors. Where the humus content is high, the isoelectric point remains always low, but where there is little humus in the complex, its isoelectric pH will increase with the progressive loss of silica, until the lateritic stage is reached.

That the process of weathering in the humid regions proceeds according to the above postulate is shown by the composition of soil colloids. The analyses of Robinson and Holmes (1924), covering 45 soil colloids from various parts of the United States, show an average ratio of silica to sesquioxides

of 2.18. This figure becomes considerably lower if the colloids from arid regions are eliminated: The soil colloids are richer in sesquioxides and poorer in silica and bases than the original rock.

The above type of weathering, which might be termed *anionic solvation and eluviation*, is the type which leads to the formation of laterites, red, yellow and brown earths, and brown forest soils.

In a previous publication (MATTSON & NILSSON, 1935) it was stated that the anionic sol complex cannot be isoelectrically precipitated during its downward movement in a soil, whose pH increases with the depth, because the ionization and negative charge of the complex will only be greater as the pH increases. But it may, nevertheless, be precipitated, not by the OH ions but by interacting with the gel complex, which in the deeper B horizon has a higher isoelectric point than the gel complex in the upper A or humus horizon. The gel complex in B will then act as a base toward the more acidic sol complex coming from the A horizon. Thus it has been found that dark colored electronegative sols may be nearly decolorized by passing through soil material from the B horizon of a brown soil as well as of a podzol profile. This type of precipitation is responsible for the chemical illuviation of acidic material, traceable in the non-podzolic profiles, notably the impregnation or organic matter in the deeper horizons (LUNDBLAD, 1934). But a large part of the anionic sol complex reaches the streams and rivers. It is largely material of this nature, which imparts a brownish color to their water. The harder well water is clear, because the negative sol is flocculated by the Ca ions.

The anionic solvation and eluviation leads to an increase in the isoelectric pH of the gel complex. The leaching of the bases leads to a decrease in the pH of the soil. When the two pH values coincide, that is, when the net base saturation of the complex is zero, the step to the other type of weathering, i.e., the *cationic solvation and eluviation*, is a short one. If the production of acids exceeds the production of bases as

under conditions of the formation of a sour humus cover, then the pH of the soil will fall below the isoelectric pH of the complex. The exchangeable cations being practically exhausted, the basic residue of the complex will become engaged, and a cationic sol complex will be mobilized, resulting in a development of the podzol profile. The cationic sol complex, being richer in basoids, will leave the gel complex richer in acidoids and with a lower isoelectric point. The lowering of the isoelectric pH will tend to oppose a further cationic solvation just as an elevation of the isoelectric pH tends to oppose a further anionic solvation (Le Chatelier's law).

Since the pH in the soil normally increases downward, the cationic sol complex, unlike the anionic complex, is always isoelectrically precipitated at a certain depth in the soil, giving rise to the B horizon of the podzol profile. The depth at which the cationic complex will precipitate will, of course, depend upon its isoelectric point, and upon the pH gradient in the profile.

We have deep and we have shallow podzol profiles. A podzol profile at Sunnersta, near Upsala, having a high water table and gley formation at 17 cm, had a pH of 3.9 at 10 cm and 5.2 at 17 cm. The B horizon is dark brown, compact with some ortstein but only about 4 cm deep. Where the pH gradient is less steep the cationic sol complex can wander to a considerable depth, if its isoelectric point is high.

According to AALTONEN (1935), precipitation takes place at a greater depth in the younger than the older podzols, that is, the B horizon grows from the bottom up. This should mean that the isoelectric point of the cationic sol complex is higher in the former than in the latter. The isoelectric point of the cationic sol complex will be determined (1) by the pH of the soil, and (2) by the isoelectric pH of the gel complex, as shown in the experimental part (comp. fig. 8 and 14). In the early stages of the process of podzolization, while the gel complex in the A horizon is still relatively rich in sesquioxides, we would expect the isoelectric point of the cationic sol com-

plex to be higher, and the complex to wander deeper, than in the older podzols. Later, as the sesquioxides become exhausted, the isoelectric point of the sol complex will be lower, and will, accordingly, be precipitated by the lower pH in the upper B horizon. Our theory will, therefore, not only give a satisfactory explanation of the fact, that the material precipitated in the upper B is more acidic than that precipitated in the lower part of this horizon, it will also explain »das Aufsteigen des B-Horizontes nach oben beim Älterwerden des Bodens» (AALTONEN, 1935).

If the podzol B horizon grows from the bottom up, as claimed by Aaltonen, where, and by what, is it stopped? Is there then a lower limit to the A horizon?

On the basis of the laws of isoelectric precipitation, and of the present status of our experimental work, we shall attempt to answer the questions as follows:

The cationic solvation and eluviation proceeds downwards from the top of the mineral soil[1], whereas the precipitation begins at a certain depth, depending upon the pH, and proceeds upwards as the cationic sol complex becomes more and more acidic with the age of the profile.[2] The »waves» will ultimately meet, that is, the zone of precipitation will border on to the zone of solvation. At this stage the cationic sol complex has become so acidic, and its isoelectric point so low, that it is precipitated at a pH immediately below that prevailing in the lowest part of the A horizon. This marks the upper limit of the B horizon. When the isoelectric pH of the gel complex in the A horizon has been reduced to a value equal to the prevailing pH in this horizon, there can be no further mobilization of a cationic complex. Where the crest of precipitation coincides with the valley of solvation there is no motion.

[1] Because of a high humus content in A_1 the solvation of sesquioxides is usually less intense in A_1 than in A_2 (JOFFE).

[2] The composition and properties of the sol complex will also vary with the seasonal fluctuations in humus formation, pH, rainfall, etc.

The process, as described, is illustrated in fig. 14. Let us assume a pH of 4 in the zone of eluviation, and let system I (0.0 gram humus) represent the conditions at the beginning. The cationic sol complex would be isoelectric at about pH 7, and would be precipitated at a depth in the profile where the pH is, let us say, about 6. Later, as the gel complex in the A horizon becomes more acidic, the conditions will be more nearly represented by system II (12.5 grams humus). The isoelectric pH of the cationic sol complex is then about 6, and would be precipitated at a depth in the profile where the pH is, let us say, about 5. Now let system III (25 grams humus) represent the conditions at an advanced stage of podzolization. The isoelectric pH of the cationic sol complex is only slightly above 4, or at about 4.2. This complex, if it were formed at all, would obviously be precipitated by the slightest increase in pH, or immediately under the zone of eluviation. A slightly more acidic system would itself be isoelectric at the assumed pH of 4, and this would mean an end to the cationic solvation and eluviation in the A horizon.[1]

The result of a still further increase in the acidoid content in the soil complex in the A horizon, through an increment of humus, is illustrated by system IV (50 grams humus) in fig. 14. The isoelectric pH of the complex will be lower than the pH of the soil, and the preceding cationic solvation and eluviation will be succeeded by an anionic solvation and eluviation. The anionic sol complex will however to a large extent be precipitated in the B horizon, in combination with the more basic gel complex there. This precipitation of primarily humic material would proceed from the upper to the lower parts of the B horizon, and would represent the beginning of the formation of the humus podzol.

[1] The pH might of course sink below 4 and keep the process going, but only for a limited length of time because there is a limit to the amount of sesquioxides present in the complex, and then, there must likewise be a limit to the acidity produced by the leachings from the humus layer. The ultimate state would therefore be the same.

We now come to the question of the lower limit of the A horizon.

With the continued production of acids in excess of bases, it seems obvious to us that the eluviation of sesquioxides must continue down into the B horizon. For if these acids are not »neutralized» in the A horizon, due to the lack of basic material, and if they are not decomposed on their way, they will pass on to the B horizon, and there ionize the sesquioxides once precipitated. If the B horizon is poor in humus, as in the case of the drier profiles (iron podzols), then the bleached horizon would simply extend downwards. But in the case of the wetter profiles, in which there is a high humus content in the B horizon, a part of the humus in combination with Al and Fe would be set free, and, as a colloidal acid, left behind. The color would therefore be dark gray to black in this case. The chemical nature of this reaction would, however, be the same as in the case of the upper bleached layer of the A horizon, to which the cationically eluviated, but blackish layer genetically belongs. The process would lead to the development of the humus podzol.

Below the layer of humus accumulation a second bleached layer might develope after the eluviation of the sesquioxides. Due to the high isoelectric point the cationic eluviation in this layer might precede the eluviation in the humous layer higher up. This second bleached layer would correspond to the B^{a_2} horizon described by Tumin (1912).

All of these layers, the humous dark as well as the bleached layers, belong to the *cationically* solvated and eluviated or podzolized horizon. It is therefore not merely a question of color and of eluviation and illuviation when the podzolized horizon is to be defined. The kind of material envolved, whether acidic or basic, is more important. The process of podzolization cannot be clearly defined without a distinction between anionic and cationic solvation and precipitation. We shall return to a discussion of this problem later in connection with our present work on humus podzols.

Aaltonen found a periodic precipitation of iron when he precipitated a ferric hydroxide sol in columns of sand, and states that this cannot by explained on the basis of isoelectric precipitation. But the isoelectric precipitation is to a certain extent autocatalytic. It must be remembered that a cationic sol is precipitated already on the acid side of its isoelectric point, especially when combining with a colloid having a lower isoelectric point, e. g., the gel complex in the sand. The initial precipitation will serve as a nucleus for a further precipitation, because the isoelectric pH of the silicate (or humate) complex, being increased through the addition of basoid, will cause the pH of the medium to be higher in the immediate neighbourhood of the complex, thus rendering the sol more unstable. We look upon such zones of a higher pH as the cause of the formation of concretions and of the horizontal streaks observed by Tamm (1920) in the B horizon of undeveloped podzols.

Summary.

The theory of the interaction of colloidal hydroxides and acids has been discussed.

The anionic and cationic sol complex, obtained at different pH in the extracts from various mixtures of soil and humus, has been studied with respect to composition and isoelectric point.

It has been found that there is a minimum of solvation at a pH which corresponds to the isoelectric point of the gel complex in the mixture.

Above this pH the sol complex is anionic and more acidic than the gel complex, whereas it is cationic and more basic than the latter at lower pH.

Applied to the process of soil formation, a distinction is made between (1) anionic solvation and eluviation leading to laterites, red and brown earths, and (2) cationic solvation and eluviation leading to podzolic soils.

Resumé.

Inledningsvis har reaktionen mellan kolloidala syror och baser berörts jämte sambandet mellan de bildade kolloidkomplexens amfotära egenskaper och deras sammansättning.

Den i dessa annaler (Mattson & Nilsson, 1935) förut behandlade undersökningen av extrakt erhållna genom utskakning i sur lösning av rostjord tillsammans med stigande mängder humus har fortsatts och utvidgats.

Sålunda har varje blandning av rostjord och råhumus utskakats i serier med varierande pH, erhållna genom tillsats av stigande mängder NaOH resp. HCl. De extrakt, som vunnits efter filtration ha blivit undersökta med hänsyn till fällningsoptimum och isoelektrisk punkt. Mängden NaOH erforderlig för neutralisation har bestämts, likaså halten av organisk substans, kiselsyra, järn och aluminium. Resultaten som äro angivna i tabell 3, ge vid handen följande:

1. Ett minimum med avseende på solvatiserad resp. löst substans existerar och har sin plats vid det pH, som motsvarar gelkomplexets isoelektriska punkt. Detta pH sjunker med stigande råhumushalt i blandningen (jämf. fig. 9, 10 och 11).

2. Mängden solvatiserad såväl basisk som sur substans tilltar både på den sura och den basiska sidan om gelkomplexets isoelektriska punkt, men förhållandet seskvioxider/organisk substans + kiselsyra stiger, om man går åt den sura sidan och avtar om man går åt den alkaliska.

3. Solkomplexet är på den sura sidan om minimiläget ett katjonkomplex, d. v. s. det har positiv laddning, medan man på den alkaliska sidan finner ett anjonkomplex, som således är negativt laddat.

Det sagda innebär, att markkomplexet har sin största stabilitet vid isoelektriska punkten. Om pH sjunker under denna punkt och urlakning samtidigt äger rum, förlorar komplexet i första hand basisk substans, medan den sura blir kvar. Stiger däremot pH över den isoelektriska punkten lösgöres

företrädesvis sur substans, medan den basiska förblir i det närmaste orörd. Vid jordmånsbildningen har man därför att skilja på:

1. *anjonisk solvation och eluviation*, som leder till laterit-, rödjords- och brunjordsbildning,
2. *katjonisk solvation och eluviation* som leder till podsolbildning.

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